THE DETERMINATION OF URANIUM AND VANADIUM IN THE CARNOTITE ORES OF COLORADO AND UTAH.

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(*Read April 17, 1913.*)

The determination of uranium in ores has become a matter of importance, due to the discovery of ores containing this element in Colorado and Utah and the constantly increasing demand for them. In these ores the uranium is associated with two to four times as much vanadium and varying amounts of silica, alumina, oxide of iron, lime and magnesia. They are practically free from phosphoric acid and sulphides, and contain very small amounts of metals precipitated by hydrogen sulphide in an acid solution. The problem thus is practically the separation of the uranium and vanadium from the alumina and oxide of iron, and their separation from each other. The first part of the problem is readily solved by the use of ammonium carbonate, which dissolves the uranium and vanadium and precipitates the oxide of iron and alumina. The separation of uranium from vanadium is more difficult, owing to the strong affinity between these elements. The volumetric method seems to offer an ideal separation as hydrochloric acid reduces the vanadium to the vanadyl condition without affecting the state of oxidation of the uranium and subsequent evaporation with sulphuric acid and titration with permanganate gives an accurate method for the determination of the vanadium. Subsequent reduction by aluminum reduces the uranium to UO_2, but it also reduces the vanadium theoretically to the state of V_2O_2, but upon the removal of the aluminum the vanadium absorbs oxygen so quickly that the actual state of oxidation is uncertain and the titration becomes unreliable. In Low's "Technical Methods of Ore Analysis," page 204, the method relies on the precipitation of the vanadium as lead vanadate in the presence of free acetic acid for its separation from the uranium, and while with great care this may be accomplished with more or less accuracy it leaves much to be desired in the way of simplicity and ease of manipulation.

The method given by Carnot[1] for the determination of vanadium by adding uranyl nitrate and precipitating the ammonium uranyl vanadate in a solution slightly acid with acetic acid lends itself admirably to the reverse determination, and in the presence of an excess of vanadic acid the uranium may be accurately and easily determined.

Ammonium uranyl vanadate is a canary yellow flocculent precipitate resembling sulphide of arsenic. It settles rapidly and is quite insoluble in a solution faintly acid with acetic acid. It must be washed with a hot solution containing about 5 c.c. of slightly acid ammonium acetate to 100 c.c. of water, as it is slightly decomposed by pure water, passes through the filter and is reprecipitated in the filtrate. Upon ignition the $V_2O_5, 2UO_3(NH_4)_2O + H_2O$ loses ammonia and water and becomes $V_2O_5, 2UO_3$. It burns readily, but should not be heated above a low red, as it fuses and becomes very insoluble. Even when not fused it dissolves with difficulty in a large excess of dilute nitric acid. Fusing the salt does not appear to change its composition or the degree of oxidation of the uranium as the weight remains constant. When fused, a little hydrofluoric acid added to the dilute nitric acid causes it to dissolve more readily.

Determination of Uranium.

Boil two grammes of the finely ground ore with 25 c.c. of strong nitric acid and 25 c.c. water for half an hour, dilute and filter. Reject the insoluble portion. Neutralize the filtrate with ammonia and after a precipitate has formed add a strong solution of ammonium carbonate in excess. A large excess of ammonium carbonate is to be avoided as it dissolves appreciable amounts of both alumina and oxide of iron. This precipitates the alumina, oxide of iron, etc., while the uranium and vanadium are dissolved. The volume of the solution should be about 250 c.c. The solution should be warm but not hot, 40°–50° C. is a good temperature. Stir constantly for fifteen or twenty minutes and allow the precipitate to settle. Decant as much as possible of the clear liquid on the filter, and finally pour

[1] "Traité d'Analyse des Substances Minerales," Vol. II, p. 791.

on the precipitate and wash it two or three times with water containing two grammes of ammonium carbonate to the 100 c.c. Evaporate the filtrate. Dissolve the precipitate in a small quantity of hot dilute nitric acid and reprecipitate as before. Filter and add the filtrate to the first one. Evaporate until the ammonium carbonate is expelled and acidulate with a few drops of nitric acid. Evaporate until the volume of the solution is about 200 c.c., transfer to a 400-c.c. beaker, and add ammonia until a precipitate appears. Add nitric acid drop by drop until the solution clears, then add 10 to 15 c.c. of ammonium acetate, made by adding 30 per cent. acetic acid to strong ammonia until the liquid is acid to litmus paper. This will require a little over three volumes of acetic acid to one volume of ammonia. The precipitate which forms immediately is the ammonium uranyl vanadate $V_2O_5, 2UO_3, (NH_4)_2O + H_2O$, mentioned by Carnot. After boiling for a few minutes it settles rapidly, leaving a clear supernatant liquid. Decant the clear liquid on a filter and wash twice by decantation with hot water containing 5 c.c. of the ammonium acetate mentioned above to 100 c.c. of water. Wash the precipitate onto the filter and wash several times with the same solution. Dissolve the precipitate adhering to the beaker in hot dilute nitric acid, pour it on the filter allowing the solution to run into a small beaker. Wash the filter with dilute nitric acid and hot water and evaporate the solution to dryness, without heating above water bath temperature. Dissolve in a little hot dilute nitric acid and add ammonia until a precipitate forms, then ammonium carbonate to dissolve the uranium and vanadium and precipitate any alumina and silica. Allow to stand until the precipitate settles, filter, wash with ammonium carbonate, acidulate the filtrate with nitric acid, boil off the carbonic acid and precipitate by ammonia and ammonium acetate as above. Filter, wash, ignite at a low red heat and weigh as $V_2O_5, 2UO_3$, which contains 74.48 per cent of U_3O_8.

The success of this method depends on the presence of more than a sufficient amount of vanadic acid to form a precipitate of the composition mentioned, and this is the case with all the ores I have seen from these localities. It is well, however, to make sure of this and therefore the filtrate from the first precipitation of ammonium uranyl vanadate should be acidulated with nitric acid and a few drops of hydrogen peroxide added. If the liquid becomes brownish yellow in color it shows an excess of vanadic acid. If it does not it is better to take a fresh portion and add a solution of vanadic acid in nitric acid. The amount to be added can be judged by the appearance of the precipitate of ammonium uranyl vanadate formed in the first instance.

Second Method for the Determination of Uranium.

In the presence of large amounts of alumina and oxide of iron an extremely accurate separation of uranium may be made by using the reaction suggested by Gooch & Havens,[2] by which aluminum chloride is precipitated in a crystalline form free from iron in a solution of equal parts of ether and the strongest hydrochloric acid saturated with hydrochloric acid gas. Havens[3] has shown that this method gives a separation of alumina from beryllium, zinc, copper, mercury and bismuth. I have found that it gives an excellent separation from uranium and vanadium and the method as worked out is as follows:

Treat two grammes of ore as directed in the method described above for the determination of vanadium and after evaporating the hydrochloric acid solution to syrupy consistency, transfer it to a narrow graduated beaker of about 100 c.c. capacity, using concentrated hydrochloric acid to wash all the solution from the larger beaker. The liquid should not exceed 20 c.c. to 25 c.c. in volume. Cool the liquid to about 15° C., and saturate it at that temperature with hydrochloric acid gas. The gas may be generated from rock salt or ammonium chloride in lumps and strong sulphuric acid and the current of gas should be constant and of considerable volume.

When the gas is no longer absorbed but passes freely through the liquid in the beaker note the volume and add an equal volume of ether. Saturation of the liquid generally increases the volume about one fifth and to obtain a satisfactory separation of alumina the volume of ether added should equal the volume of the saturated solution. Continue passing the gas until the solution is again saturated, being careful to keep the temperature of the solution close

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[2] Gooch, "Methods of Chemical Analysis," p. 204.

[3] *Loc. cit.*, pp. 216, 217.

to 15° C. Hydrous aluminum chloride is precipitated together with lead chloride, while iron, uranium, vanadium, etc., remain in solution. Prepare an equal volume of hydrochloric acid and ether saturated as described above at 15° C. to wash the precipitate of aluminum chloride.

Filter on a Gooch crucible, allowing the solution to run into a beaker in a bell-jar and wash with the prepared solution. Heat the filtrate and washings carefully, evaporate to syrupy consistency and make an ether separation in the usual way. The ethereal solution contains the ferric chloride and any molybdenum that may be in the ore, while the acid solution contains the uranium, vanadium, lime, etc. Evaporate the solution nearly to dryness, replace the hydrochloric acid by nitric acid, and evaporate to dryness at water bath temperature. This oxidizes the vanadium and uranium to the vanadic and uranic conditions. Add a few drops of nitric acid and dilute the solution, add ammonia until a permanent precipitate forms, then excess of ammonium carbonate to dissolve the uranium and vanadium, and filter to get rid of any small amounts of alumina, and oxide of iron that may not have been removed by the operations described above. Determine the uranium as described in the first method as uranyl vanadate.

DETERMINATION OF VANADIUM.

Boil 2 grammes of the finely ground ore with 10 c.c. of nitric acid and 10 c.c. of water, add hydrochloric acid in excess, evaporate to dryness, redissolve in hydrochloric acid, dilute and filter. Reject the insoluble matter. Evaporate the filtrate to syrupy consistency and make an ether separation to get rid of the iron. Evaporate the hydrochloric acid solution very low, add 25 c.c. or 30 c.c. hydrochloric acid and repeat the evaporation several times to insure the reduction of the vanadium to vanadyl chloride. Add 5 c.c. strong sulphuric acid and evaporate until fumes of sulphuric acid are given off. Cool, dissolve in water, and titrate at a temperature of about 60°–70° C. with permanganate solution in a volume of about 100 c.c. The iron factor of the permanganate multiplied by 1.6342 gives the V_2O_5, taking vanadium as 51.0.

PHILADELPHIA, April, 1913.